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Acyclic (η^5-Dienyl)tricarbonyliron(1+) Cations Generated *in Situ* in the Presence of Molecular Sieves: Modified Reactivity with Primary and Secondary Alcohols

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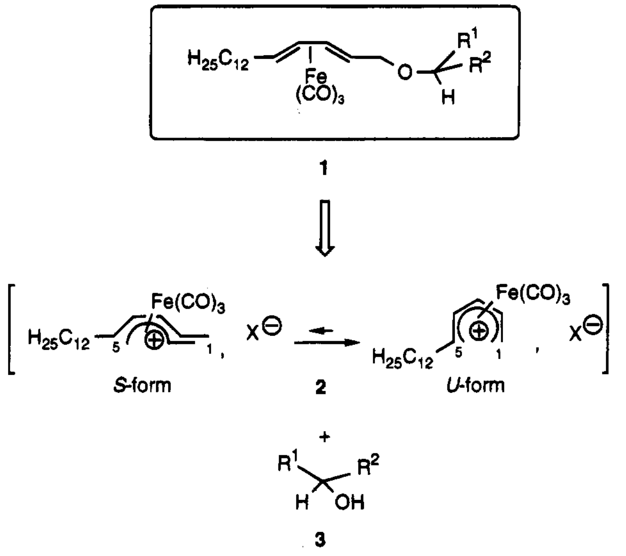
Introduction

Over the past decade, η^4-dienyl tricarbonyliron complexes have proved extremely useful as intermediates in organic synthesis.[1] We reasoned that, since the η^4-butadienyl tricarbonyliron moiety greatly stabilizes a carbocation located at the α position of the coordination site,[2] ethers of type **1** might be readily obtained by regioselective nucleophilic addition of alcohols **3** *only at position 1* of the cation **2** (Scheme 1). We report in this work, on the easy and general access to unsymmetrically disubstituted complexed ethers of type **1**.

The regioselectivity control of this addition would present a challenge since it is well-known that the nature of the nucleophiles, the reaction conditions, and, not least, the nature of the dienyl ligands are major factors.[1] Moreover, acyclic organometallic *U*-cations react at *both termini* (1 and/or 5) while *S*-cations react regioselectively.[1]

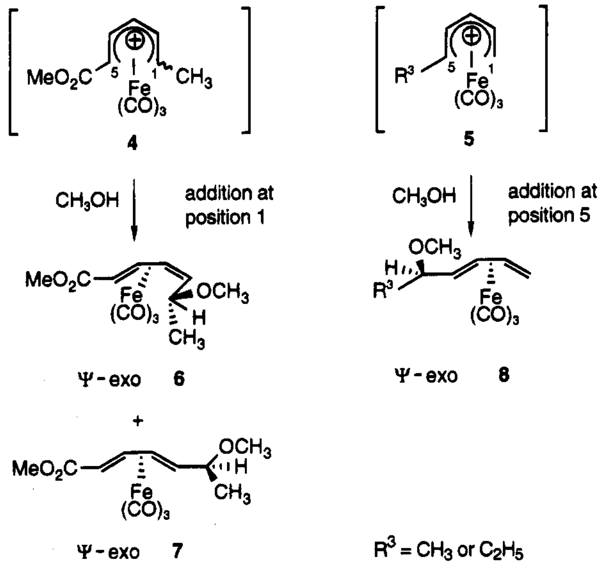
In the case of alcohols as nucleophiles, the sparse literature data available describe only the anti addition of *the simplest primary methyl alcohol* with *isolated acyclic cations*.[3−5] Monosubstituted cations **4** and **5**[3] afford the ether adducts **6**−**8** arising from a charge and/or an orbitally controlled addition[6] (Scheme 2). The electron-withdrawing methoxycarbonyl-substituted cation **4** gives rise to mixtures of the *(E,Z)*- and *(E,E)*-Ψ-exo complexes **6** and **7**[3a] (addition at terminus 1). On the other hand, the electron-donating monoalkyl-substituted cation **5**, *structurally related to* **2**, affords the *monosubstituted* Ψ-exo ether **8** arising from the *undesired* addition of MeOH at position 5.[3b]

Scheme 1



X⊖ = PF_6⊖ or BF_4⊖ ; R^1 or R^2 = H or ≠ H

Scheme 2



Given these results, we chose to examine the reactivity of the butyl-substituted cation **12**, as a model compound for **2**, toward various primary and secondary alcohols **3** (Scheme 3). To further enhance the utility of our proposed *one-step* etherification of **10**[7] via **12**, we imposed two contraints: (1) the *in situ* generation[8] of **12** in the presence of alcohols **3** and (2) the promotion of their nucleophilic addition toward only terminus 1 of **12** affording ethers of type **13b** instead of type **13a**. For that purpose, "*ethereal aqueous tetrafluoroboric acid in the presence of activated molecular sieves* (MS)" was revealed as a novel and particularly interesting acidic system. These conditions promoted the *exclusive formation* of type **13b** complexed ethers of requisite regiochemistry.

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(1) (a) Koerner Von Gustorf, E. A.; Grevels, F. W.; Fisher, I. *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vols. I and II. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon Press: Oxford, 1982. (c) Pearson, A. J. *Metallo-Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1985. (d) Franck-Neumann, M. *Organometallics in Organic Synthesis*; Tom Dieck, H., Ed.; Springer-Verlag: Berlin, 1987. (e) Grée, R. *Synthesis* **1989**, 341.

(2) (a) Fischer, E. O.; Fischer, R. D. *Angew. Chem.* **1960**, *72*, 919. (b) Palotai, I. M.; Stephenson, G. R.; Ross, W. J.; Tupper, D. E. *J. Organomet. Chem.* **1989**, *364*, C11. (c) Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 339.

(3) Mosset, P. Ph.D. Thesis, University of Rennes, 1984. (b) Mahler, J. E.; Gibson, D. H.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3959.

(4) (a) Donaldson, W. A.; Bell, P. T.; Jin, M. J. *J. Organomet. Chem.* **1992**, *441*, 449. (b) Donaldson, W. A.; Jin, M. J.; Bell, P. T. *Organometallics* **1993**, *12*, 1174. (c) Donaldson, W. A.; Jin, M. J. *Bull. Soc. Chim. Belg.* **1993**, *102*, 297.

(5) Isolated (η^5-dienyl)tricarbonyliron(1+) cations are efficiently prepared by dehydration of the corresponding alcohols: (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955. (b) Donaldson, W. A.; Ramaswamy, M. *Synth. React. Inorg. Met. Org. Chem.* **1987**, *17*, 49. (c) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *J. Organomet. Chem.* **1979**, *174*, 297.

(6) An additional case has been described following the same trend of reactivity and regioselectivity as **4**: Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2134.

(7) (a) Pinsard, P.; Lellouche, J. P.; Beaucourt, J. P.; Grée, R. *Tetrahedron Lett.* **1990**, *31*, 1137. (b) Pinsard, P.; Lellouche, J. P.; Beaucourt, J. P.; Toupet, L.; Schio, L.; Grée, R. *J. Organomet. Chem.* **1989**, *371*, 219.

(8) Very few studies devoted to the reactivity of *in situ-generated acyclic* (η^5-dienyl)tricarbonyliron(1+) cations are known. They involve the solvolysis of iron-complexed dinitrobenzoates[17] and the Lewis acid-mediated carbon−carbon[18] and carbon−phosphorus[7] bond formation starting from acyclic (η^4-dienyl)tricarbonyliron(0) acetates.

0022-3263/94/1959-4693$04.50/0
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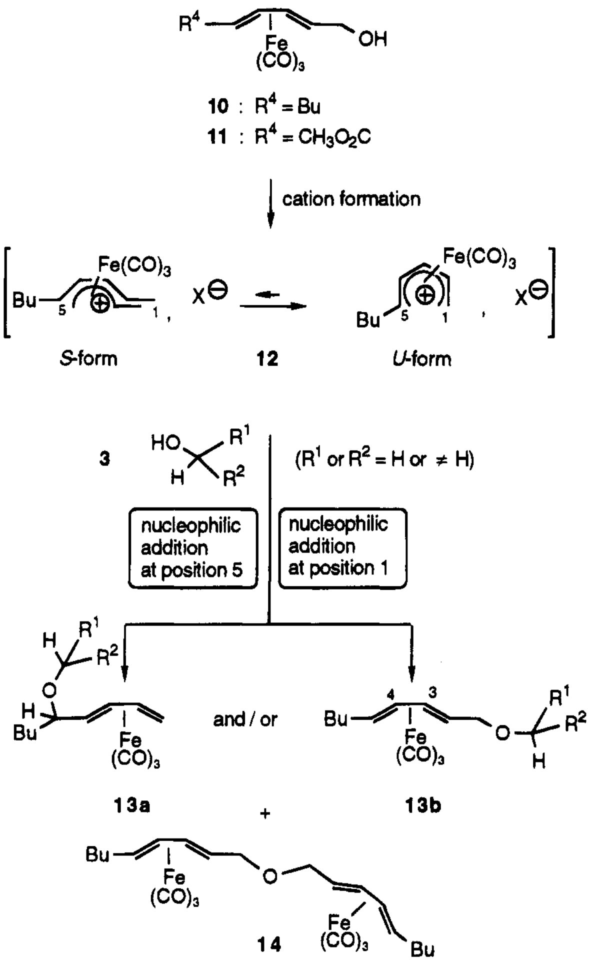
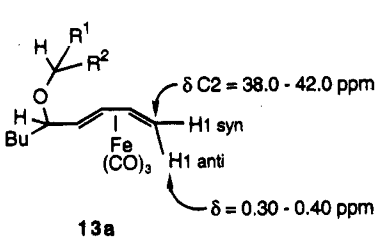
Scheme 3



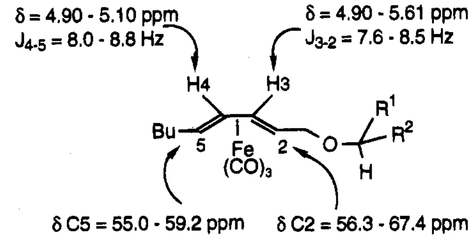
Etherification of 10 Using Various Aqueous Acidic Conditions

A preliminary set of trials involves the use of activated 4 Å molecular sieves (Table 1, entries 1–6) using the following protocol:

Alcohol **3** dissolved in ether in the presence of the molecular sieves is mixed at 20 °C with aqueous HBF_4. The alcohol **10**[7] is then slowly added (3 h) using a syringe pump, in order to minimize the formation of the dimeric species **14** (<5%). The corresponding ethers of type **13b** are isolated. In each case, whatever the primary (entry 1) or secondary (entries 2–6) structures of **3**, the unsymmetrical complexed ethers **15b–20b** of type **13b** (addition at terminus 1 of **12**) are always isolated accompanied by some decomplexation products and unreacted **10**. Adduct yields are poor to good varying from 27% in the case of the very encumbered (−)-menthol [(−)–**20**] (entry 6) up to 83% in the case of *R*-**17** (entry 3). Evidence for the (*E,E*)-stereochemistry and disubstitution of the complexed conjugated diene moiety present in these ethers is supported by the multiplicity (d or dd) of the H_3/H_4 resonance signals observed with or without irradiation of H_2/H_5, the coupling constant values measured for $J_{3\text{-}2}/J_{4\text{-}5}$ and the resonance signal values of C_2/C_5[9] (see the Figure 1 below). Additionally, lack of the highly shielded resonance signal of H_{1anti} and of C_1 (^{13}C-NMR) in **13a** is consistent with the proposed **13b**-type structures.[9]



13a



13b

Figure 1.

Yields and the alcohol structures cannot be correlated in a simple way to steric effects (entries 2–6 versus entry 1). The more encumbered (−)-menthol [(−)-**20**] still gives a 27% yield of **20b** (entry 6). Interestingly, there is no chiral discrimination[10] of **12** when using the chiral alcohols *R*-**16**, *R*-**17**, and (−)-**20**.

The synthetic potential and limitations offered by acidic conditions related to the aqueous HBF_4/4 Å molecular sieves system were further examined. Starting from **10** and **18**, the entry 7 shows that aqueous HBF_4 can be replaced by aqueous H_2SO_4 without lowering the yield of **18b** (entry 7 versus entry 4) while CF_3COOH (entry 8) and aqueous HPF_6 (entry 9) do not afford even traces of **18b**. The choice of the solvent is also of great importance since replacement of Et_2O for $ClCH_2CH_2Cl$ greatly lowers the yield of **18b** from 40% (entry 4) to 17% (entry 10). No ether adducts arising from condensation of *R*-**16** with the electronically deficient complexed alcohol **11** are isolated (entry 11) and alcohol **11** is recovered unchanged after treatment. It follows that our system would be able to dehydrate acyclic iron complexed alcohols in a rather chemoselective manner depending on their substitution patterns. Selective processes involving **10** rather than **11** like hydrophobic or dipole–dipole interactions and/or the accessibility to the acidic sites on the molecular sieves surface could account for this result. This particular question must be addressed by studying a wider range of variously substituted complexed alcohols.

The crucial role played by the molecular sieves in controlling regioselectivity is clear. The trial involving **10** and *R*-**16** using *anhydrous $MgSO_4$* instead of 4 Å molecular sieves gives a 19/81 mixture of the two ethers **16a** + **16b** (60% yield, entry 12) as seen by high-field ^1H-NMR. The classical water-scavenging properties of the molecular sieves cannot explain these results (compare entry 12 versus entry 2).

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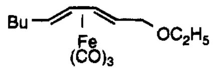
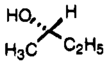
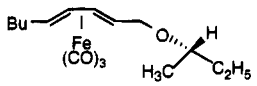
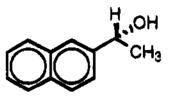
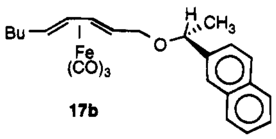
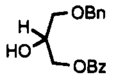
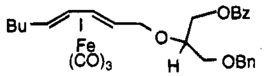
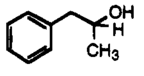
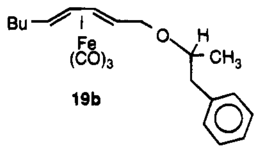
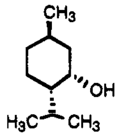
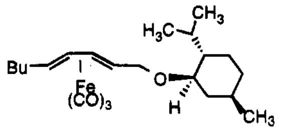
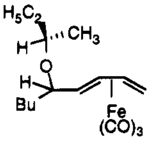
(9) (a) Marks, T. J. *The Organic Chemistry of Iron*; Koerner von Gustorf, E. A.; Grevels, F. W.; Fischer, I.; Eds.; Academic Press: New York 1981; Vol. I, pp 113–144. (b) Pearson, A. J. *Metallo-Organic Chemistry*; John Wiley and Sons: New York 1985, pp 262–264.

(10) Kinetic and/or thermodynamic discrimination has been observed during reactions involving unsymmetrical *cyclic* (η^5-dienyl)iron(1+) cations with various nucleophiles: Pearson, A. J. *Comprehensive Organic Synthesis: Selectivity, Strategy And Efficiency In Modern Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York 1991; Vol. IV, pp 687–689.

Table 1. Etherification of the *in Situ*-Generated Acyclic (η^5-Pentadienyl)tricarbonyliron(1+) Cation 12

entry	iron complexed alcohol	condensing alcohol	etherification / isomerization conditions	adduct (s) structure (s) [c]	yield of isolated adduct (%)
1	10	C_2H_5OH **15**	SdC = aqueous HBF_4, 4Å MS, ethyl ether, 20 °C, 18 h [a]	 **15b**	40
2	"	 *R*-**16**	"	 **16b**	33
3	"	 *R*-**17**	"	 **17b**	83
4	"	 **18** [b]	"	 **18b**	40
5	"	 **19**	"	 **19b**	44
6	"	 (-)-**20**	"	 **20b**	27
7	"	**18**	SdC (aqueous H_2SO_4)	**18b**	40
8	"	"	SdC (CF_3CO_2H)	—	0
9	"	"	SdC (aqueous HPF_6)	—	0
10	"	"	SdC (1,2-dichloroethane)	**18b**	17
11	**11**	*R*-**16**	$\boxed{\text{SdC}}$	—	0
12	**10**	"	SdC ($MgSO_4$)	 **16a** + **16b** : 19 / 81	60
13	"	"	SdC (3Å MS)	**16b**	87
14	"	"	SdC (5Å MS)	major product **14** + traces of **16b**	< 5
15	"	"	SdC (10Å MS)	**16b**	58
16	"	**18**	SdC (3Å MS)	**18b**	23
17	"	"	SdC (5Å MS)	major product **14** + traces of **18b**	< 5
18	"	"	SdC (10Å MS)	**18b**	7

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[a] "SdC" is relative to standard conditions. The modified parameter of "SdC" is underlined in the table. [b] **18** is synthesized by benzoylation of the commercially available 3-(benzyloxy)-2-hydroxy-1-propanol (see the Experimental Section). [c] Lack of the shielded signal of H_{1anti} in **13a**-type ethers gives a NMR-based lower limit of detection of 4-5% for these minor adducts.

Apart from likely differential adsorptions of reactants on molecular sieves, the effect of the molecular sieves pore sizes can be appreciated when using 3 Å, 5 Å, and 10 Å molecular sieves. The results from the two model etherification reactions involving **10** with *R*-**16** (entries13–15) but also **10** with the more hindered alcohol **18** (entries 16–18) are presented in Table 1.

The regioselectivity of the addition is independent of pore size (compare entries 13–15 and 16–18 with entries 1–6). The etherification process always results in the formation of the adducts **16b** and **18b** *of **13b** and not **13a** type.*

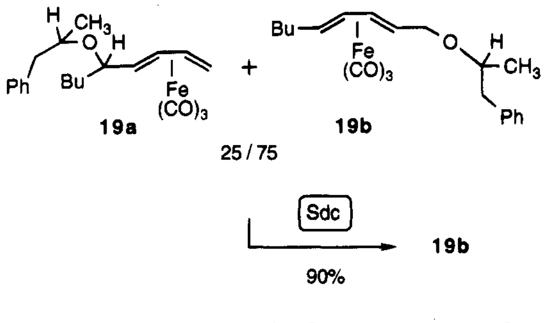
Moreover, for a given alcohol *R*-**16** or **18**, the etherification yields vary greatly with the pore size. Simply replacing 4 Å molecular sieves (entry 2) with 3 Å molecular sieves (entry 13) increases the yield of **16b** from 33 to 87%. Even the 10 Å molecular sieves gives a better yield of **16b** (58%, entry 15) than do 4 Å molecular sieves. However, this trend is not followed by the reaction involving **18** since the 4 Å molecular sieves affords **18b** in a better yield (40%, entry 4) than with either 3 Å (23%, entry 16) or 10 Å molecular sieves (7%, entry 18).

Clearly, for a given molecular sieves, the structural differences between *R*-**16** and **18** have a profound effect on the yields of **16b** and **18b**, respectively (compare entry 13 versus 16 and entry 15 versus entry 18). These are most probably due to differential interactions and/or adsorptions on the molecular sieves surface of *R*-**16** and **18**.

The 5 Å molecular sieves (which is the only molecular sieves containing a divalent cation, Ca^{2+}) must be considered apart since the dimer **14** is always isolated as the major compound accompanied with traces of **16b** and **18b**. The particular composition[11] and/or structure of this molecular sieves is certainly of importance with regard to diffusion processes of the reaction partners.

Additional Result Involving 12

A new reactivity aspect involving the cation **12** can be also put into evidence through the experiment described in eq 1. During this experiment, **12** is generated not as previously done from the alcohol **10** but from the mixture of ethers **19a** + **19b**.[12,13] The feasibility of the putative equilibrium **13a** ⇄ **13b** interconverting a pair of regioisomeric ethers must be examined here considering the following experiment.



(eq 1)

When this mixture of ethers was treated with the aqueous HBF_4/4 Å molecular sieves system, it selectively gave only the regioisomer **19b** (90% yield) without any trace of **19a**.

19b is certainly the most stable of these two regioisomers under these experimental conditions. Most likely going through **12**, the inter- or intramolecular nature of the isomerization remains to be established. Nevertheless, more work is obviously necessary in order to appreciate the scope of such an isomerization since it opens new valuable mechanistic questions dealing with the chemistry of η^5-tricarbonyliron cationic complexes.

Our reported molecular sieves-assisted etherification reaction of the iron complexed alcohol **10** is unique since the regiochemistry of the reaction is *not only modified but selectively controlled by the presence or the absence of the molecular sieves*.[14] Moreover, Dreiding molecular models of **10**, **18**, or (−)-**20** clearly shows that adsorption of these partners cannot occur *inside* the size-defined channels but rather must occur at the *outer surface* of molecular sieves-truncated cavities. This implies that accessibility to the molecular sieves acidic sites and diffusion-controlled processes[15] are likely to play major roles in the etherification here reported.

Conclusion

The new acidic system *ethereal aqueous HBF_4 in the presence of molecular sieves* allows the regiochemically controlled etherification of the butyl-substituted iron-complexed alcohol **10** with various primary and secondary alcohols. Particularly noteworthy is that the organometallic cation **12** is *generated in situ* in the presence of molecular sieves and alcohols **3**. Nucleophilic addition of **3** is always observed at its *less encumbered terminus 1*[16] with yields varying from modest to good. The complexation of **12** on the *outer surface* of the molecular sieves most likely accounts for its modified reactivity. Additionally, two other valuable points which are highlighted in this work include the acid-mediated isomerization of the complexed ether **19a** in the mixture **19a** + **19b** affording only **19b** by an inter-/intramolecular mechanism which remains to be clarified and, after decomplexation of **13b**, the potentially easy and general access to (*E,E*)-conjugated dienyl ethers. Interestingly, this preparation using acidic conditions complements the well-known Williamson ether synthesis requiring strongly basic media.

Experimental Section

IR spectra of samples were obtained either as KBr pellets (for solids), as film (for oils), or in $CDCl_3$ solution. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were obtained in $CDCl_3$.

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[11] 3, 4, and 10 Å (13X type) molecular sieves contain, respectively, monovalent Na^+ or K^+ cations ($0.6K_2O{:}0.4Na_2O{:}1.0Al_2O_3{:}2.0SiO_2{:}xH_2O$), ($1.0Na_2O{:}1.0Al_2O_3{:}2.0SiO_2{:}xH_2O$), ($1.0Na_2O{:}1.0Al_2O_3{:}2.8SiO_2{:}xH_2O$) while 5Å molecular sieves contain additionally the divalent Ca^{2+} cation ($0.8CaO{:}0.20Na_2O{:}1.0Al_2O_3{:}2.0SiO_2{:}xH_2O$).

[12] A related acid-mediated demethoxylation route to these organometallic cations from the corresponding complexed methyl ethers is known: (a) Birch, A. J.; Haas, M. A. *J. Chem. Soc. C* **1971**, 2465. (b) Birch, A. J.; Chauncy, B.; Kelly, L. F.; Thompson, D. J. *J. Organomet. Chem.* **1985**, *286*, 37. (c) Birch, A. J.; Haas, M. *Tetrahedron Lett.* **1968**, 3705.

[13] The mixture **19a** + **19b** (25/75, 67%) has been prepared by a one-step condensation of **19** with **10** using anhydrous $ZnCl_2$ in CH_2Cl_2: Guillou, C.; Lellouche, J. P. Unpublished results. Interestingly, the obtention of this mixture but also the other one, **16a** + **16b** (entry 12), *after* purification on silica gel excludes its potential isomerizing role of **13a**-type adducts toward the *exclusive* formation of **13b**-type ones. Additionally, NMR analysis of *crude* **17b** before silica gel purification shows the exclusive presence of **17b** accompanied with traces of dimer **14**.

[14] (a) Tottie, L.; Baeckström, P.; Moberg, C.; Tegenfeldt, J.; Heumann, A. *J. Org. Chem.* **1992**, *57*, 6579 and references cited therein. (b) Lem, G.; Kaprinidis, N. A.; Schuster, D. I.; Ghatlia, N. D.; Turro, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 7009.

[15] (a) Rees, L. V. C. *Chem. Ind.* **1984**, p 252–257. (b) Dyer, A. *An Introduction to Zeolite Molecular Sieves*; John Wiley and Sons: New York 1988, pp 87–102.

[16] Agreeing with data[7,17,18] obtained in *homogeneous media*, this regioselectivity could be ascribed to reaction of sole *S*-**12**. Nevertheless, one cannot exclude a regioselective addition of *U*-**12** followed by isomerization of the so-obtained (*E,Z*)-complexes in these acidic conditions. Additionally, it is speculative to ascribe this regioselectivity to *U*- or *S*-**12** when involving molecular sieves as a main *heterogeneous* partner.

[17] (a) Clinton, N. A.; Lillya, C. P. *J. Chem. Soc., Chem. Commun.* **1968**, 579–580. (b) Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3065.

[18] Uemura, M.; Minami, T.; Yamashita, Y.; Hiyoshi, K.-i.; Hayashi, Y. *Tetrahedron Lett.* **1987**, *28*, 641.

Chemicals shifts are given as δ values (ppm) with reference to Me_4Si as an internal standard. Mass spectra were done on a Finnigan-Mat 4600 spectrometer. HRMS spectra were recorded at CRMP (University of Rennes I). Elemental analyses were performed at the ICSN, CNRS, Gif-sur-Yvette. All flash chromatography was performed on Merck silica gel (40–60 mesh) at medium pressure (200 mbar). TLC was done on Merck silica gel plates ($60F_{254}$) with a fluorescent indicator. MS (Aldrich) were activated before use by drying at 300 °C (18 h, 0.1 mmHg).

(±)-1-(Benzoyloxy)-3-(benzyloxy)-2-propanol (18). To a solution of (±)-3-(benzyloxy)-1,2-propanediol (1.31 mL, 8.23 mmol) in dry pyridine–CH_2Cl_2 (1/1) (30 mL) was added benzoyl chloride (1.02 mL, 9.00 mmol). The reaction mixture was stirred at −78 °C under nitrogen for 2 h. After solvent evaporation, the residue was extracted with CH_2Cl_2 (3 × 15 mL) and water (1 × 20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated. Flash chromatography of the residue (elution with AcOEt–heptane 25/75) provided 1.57 g of **18** as a colorless oil (67% yield): IR (NaCl) 3600–3400, 1720, 1110 cm^{-1}; ^{1}H-NMR δ 2.40 (br s, 1H, OH, exchangeable with D_2O), 3.59 (dd, 1H, $J = 9.7, 5.5$ Hz), 3.65 (dd, 1H, $J = 4.2$ Hz), 4.15 (m, 1H), 4.45 (dd, 2H, $J = 9.0$ Hz), 4.60 (s, 2H), 7.35–8.02 (m, 10H); ^{13}C-NMR δ 66.0, 69.1, 71.0, 73.6, 127.8, 127.9, 128.5, 129.0, 130.2, 133.2, 137.8, 166.7; MS (CI, NH_3) *m/z* 304 $[M + NH_4]^+$, 287 $(MH)^+$. Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.32; H, 6.29; O, 22.37. Found: C, 70.78; H, 6.17; O, 22.86.

Etherification of 10. Typical Experimental Procedure. The complexed alcohol **10** (107.0 mg, 0.384 mmol) dissolved in anhydrous ether (5 mL) was added dropwise under nitrogen during 2.5 h to a mixture of activated 4 Å molecular sieves[11] (2.0 g), alcohol **3** (0.764 mmol), and 62.0 μL of aqueous fluoroboric acid solution (48% wt, 0.46 mmol). The mixture was stirred for 18 h at 20 °C. The molecular sieves were removed by filtration through Celite. Medium evaporation afforded an oil which was purified by flash chromatography (elution with 5% AcOEt in heptane) to provide the corresponding ethers **13**.

Tricarbonyl[(2–5-η^4)-(2*E*,4*E*)-1-(ethyloxy)nonadiene]iron (15b): IR ($CHCl_3$) 2020, 1965, 1120 cm^{-1}; ^{1}H-NMR δ 0.90 (t, 3H, $J = 7.0$ Hz), 1.10 (m, 1H), 1.20 (m, 1H), 1.25 (t, 3H, $J = 7.0$ Hz), 1.35 (m, 4H), 1.60 (m, 2H), 3.25 (dd, 1H, $J = 4.5, 10.0$ Hz), 3.45 (m, 1H), 3.60 (dd, 1H, $J = 8.0, 10.0$ Hz), 5.00 (dd, 1H, $J = 8.2, 5.1$ Hz), 5.15 (dd, 1H, $J = 7.8$ Hz); ^{13}C-NMR δ 13.5, 14.9, 22.0, 33.6, 33.9, 56.9, 64.7, 65.7, 71.8, 82.9, 84.9, 210.0; EIMS *m/z* 308 $[M]^+$, 280, 252, 224; HRMS calcd for $C_{14}H_{20}O_4Fe$ 308.0710, found 308.0700.

Tricarbonyl[(2–5-η^4)-(2*E*,4*E*)-1-[(1(*R*)-methylpropyl)oxy]nonadiene]iron (16b): IR ($CHCl_3$) 2020, 1965, 1150 cm^{-1}; ^{1}H-NMR δ 0.90 (m, 6H), 1.05 (d, 3H, $J = 6.1$ Hz), 1.10 (m, 1H), 1.20 (m, 1H), 1.35 (m, 5H), 1.40 (m, 4H), 1.60 (m, 2H), 3.20–3.60 (m, 3H), 5.01 (dd, 1H, $J = 8.2, 5.1$ Hz), 5.15 (dd, 1H, $J = 7.6$ Hz); ^{13}C-NMR δ 12.3, 17.7, 20.6, 27.6, 32.3, 32.6, 55.0, 55.1, 56.3, 56.5, 63.3, 68.2, 81.4, 81.7, 83.5, 83.8, 215.0; HRMS calcd for $C_{16}H_{24}O_4Fe$ 336.1023, found 336.1026.

Tricarbonyl[(2-5-η^4)-(2*E*,4*E*)-1-[[1(*R*)-(2-naphthyl)ethyl]oxy]nonadiene]iron (17b): IR (NaCl) 2040, 1965, 1100 cm^{-1}; ^{1}H-NMR δ 0.90 (t, 3H, $J = 7.0$ Hz), 1.10 (m, 1H), 1.20 (m, 1H), 1.35 (m, 4H), 1.51 (d, 3H, $J = 5.7$ Hz), 1.60 (m, 2H), 3.25 (m, 2H), 3.50 (m, 2H), 4.58 (m, 1H), 5.00 (m, 1H, $J = 8.8, 5.1$ Hz), 5.61 (m, 1H, $J = 8.5$ Hz), 7.45 (dd, 3H), 7.70 (s, 1H), 7.88 (dd, 3H); ^{13}C-NMR δ 16.2, 24.6, 26.4, 36.2, 36.6. 59.1, 59.2, 67.2, 67.4, 72.3, 72.7, 80.1, 80.6, 85.1, 85.4, 87.3, 87.5, 126.5, 127.4, 128.1, 128.4, 130.1, 130.2, 130.9, 135.4, 135.7, 143.5, 143.8, 214.3; EIMS *m/z* 434 $[M]^+$, 350, 263, 155; HRMS (molecular ion not observed) calcd for $C_{23}H_{26}O_3Fe$ 406.1231 [M − 1CO], found 406.1240; calcd for $C_{21}H_{26}OFe$ 350.1332 [M − 3CO], found 350.1352.

Tricarbonyl[(2–5-η^4)-(2*E*,4*E*)-1-[2-[[1-(benzoyloxy)-3-(benzyloxy)-propyl]oxy]nonadiene]iron (18b): IR (NaCl 1990, 1745, 1240 cm^{-1}; ^{1}H-NMR δ 0.90 (m, 3H), 1.05 (m, 1H), 1.12 (m, 1H), 1.35 (m, 4H), 1.60 (m, 2H), 3.60 (m, 2H), 3.82 (m, 2H), 4.35 (m, 1H), 4.45 (dd, 1H), 4.55 (m, 3H), 4.98 (m, 1H, $J = 8.0, 5.0$ Hz), 5.15 (m, 1H, $J = 8.0$ Hz), 7.30–7.96 (m, 10H); ^{13}C-NMR δ 13.5, 22.0, 33.6, 33.9, 56.6, 64.2, 64.8, 69.5, 71.8, 71.9, 73.3, 76.2, 76.3, 82.7, 82.9, 85.0, 127.4, 128.1, 129.4, 132.7, 166.0, 211.6; EIMS *m/z* 492, 464, 341. Anal. Calcd for $C_{29}H_{32}O_7Fe$: C, 63.50; H, 5.83. Found: C, 63.74, H, 5.97.

Tricarbonyl[(2–5-η^4)-(2*E*,4*E*)-1-[[2-(3-phenylpropyl)oxy]nonadiene]iron (19b). 19b, when prepared by isomerization of **19a**, was obtained according to the typical procedure but replacing **10** by the mixture **19a** + **19b**: IR (NaCl) 2040, 1965, 1120 cm^{-1}; ^{1}H-NMR δ 0.90 (t, 3H, $J = 7.0$ Hz), 1.05 (m, 1H), 1.10 (d, 3H, $J = 6.1$ Hz), 1.15 (m, 1H), 1.40 (m, 4H), 1.60 (m, 2H), 2.55 (dd, 1H, $J = 12.8, 6.0$ Hz), 2.90 (dd, 1H, $J = 6.0, 13.0$ Hz), 3.40–3.70 (m, 3H), 4.90–5.10 (m, 2H), 7.10–7.30 (m, 5H); ^{13}C-NMR δ 13.5, 19.3, 22.0, 33.6, 33.9, 42.9, 57.4, 57.6, 64.6, 69.8, 70.0, 71.8, 82.6, 82.8, 84.7, 84.8, 125.8, 127.9, 129.2, 138.7, 211.7; EIMS *m/z* 398 $[M]^+$, 270, 342, 314; HRMS (ion not observed) calcd for $C_{18}H_{26}OFe$ [M − 3CO] 314.1332, found 314.1323.

Tricarbonyl[(2–5-η^4)-(2*E*,4*E*)-1-[[(1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl]oxy]nonadiene]iron (20b): IR (NaCl) 2040, 1965, 1080 cm^{-1}; ^{1}H-NMR δ 0.8 (d, 6H, $J = 6.0$ Hz), 0.9 (m, 9H), 1.05–2.00 (m, 14H), 2.05 (d, 2H), 2.25 (m, 2H), 3.00 (m, 2H), 3.15 and 3.45 (m and dd, 1H), 3.55 and 3.75 (2 dd, 1H), 5.05 (m, 2H), 5.15 (m, 2H); ^{13}C-NMR δ 13.6, 15.9, 16.1, 20.7, 21.9, 23.0, 23.1, 25.2, 25.4, 30.0, 31.3, 33.6, 33.9, 34.2, 40.2, 56.3, 56.4, 57.4, 57.9, 64.6, 64.7, 69.6, 69.8, 78.7, 79.0, 82.6, 82.8, 84.8, 85.0, 210.0; EIMS *m/z* 418 $[M]^+$, 390, 361, 334; HRMS calcd for $C_{22}H_{34}O_4Fe$ 418.1806, found 418.1807.

Tricarbonyl[(1–4-η^4)-(2*E*,4*E*)-5-[(1*R*-methylpropyl)oxy]nonadiene]iron (16a). Spectral data of **16a** came from analysis of the inseparable mixture **16a** + **16b**. Data of pure **16b** are available above: IR (NaCl) 2046, 1967, 1083 cm^{-1}; ^{1}H-NMR δ 0.35 (d, 1H, $J = 10.1$ Hz), 1.40–1.70 (m, 10H), 1.80 (d, 1H, $J = 10.1$ Hz), 5.00 (m, 1H), 5.05 (m, 1 H); ^{13}C-NMR δ 14.1, 15.5, 22.7, 27.3, 36.5, 40.3, 63.9, 64.7, 80.9, 81.6, 87.1, 210.0; EIMS *m/z* 336 $[M]^+$, 308, 280.

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Supplementary Material Available: Copies of ^{1}H-NMR spectra of **15b–20b** and ^{13}C-NMR spectra of **15b**, **18b**, and **19b**; IR and NMR data with peak assignments of **18**, **16a**, **15b–20b** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.